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Relaxor Ferroelectrics for Electrostrictive Transducers

Quarterly Report

MATERIALS SELECTION AND PROCESSING

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RESEARCH AND DEVELOPMENT PROGRAM

Electrostrictive Materials Selection Criteria

In order to establish an effective basis for selecting electrostrictive material compositions for use in sonar transducers⁽¹⁾ some useful criteria for this application have been summarized:

1) **Enhanced Electromechanical Sensitivity**

Relaxor materials possess high sensitivity with electric field induced strain levels $> 0.03\%$.

2) **Appropriate Operating Temperature Range (0-30°C).**

Variation of T_m by compositional control within the three families (PMN-PT), (PNN-PT-PZ), (PLZT) in order to optimize structure-property studies of electrostriction within a thermal range appropriate for Navy sonar applications.

3) **Minimized Hysteresis**

Operation in the electrostrictive region for all selected compositions where both dielectric P-E and electro-mechanical S-E response is primarily anhysteretic.

Materials Selection

A. **Type I. $Pb(B_1B_2)O_3$ Based Electrostrictors**

The $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ system is among the most studied of all relaxor ferroelectric systems.⁽²⁾ Compositions within this system show that the role of $PbTiO_3$ ($T_c \sim 490^\circ C$) shifts the T_m upwards by about $5^\circ C/mol\%$ addition. A morphotropic phase boundary (MPB) separating pseudo-cubic and tetragonal phases exists at approximately 33% $PbTiO_3$.⁽⁴⁾ Near this MPB the dielectric maximum K_{max} is increased while the dispersive dielectric response is decreased, exhibiting normal ferroelectric behavior beyond the MPB ($PT \geq 35\%$).

By classifying according to their polarization/polar behavior, relaxor ferroelectrics in the PMN-PT system can be put into three groups for application. These regions are: I. Electrostrictive, II. Micro-Macro, and III. Macro-Polar. For reasons outlined initially in the proposal, (e.g., they exhibit significantly large strains [d_{33}], high force capability [higher K_s^+], and minimal hysteresis with faster response, etc.), Group I Electrostrictive PMN-PT relaxor ferroelectric compositions were chosen

(a) **PMN-PT**

General formula: $(1-x) Pb(Mg_{1/3}Nb_{2/3})O_3$ - $xPbTiO_3 \equiv PMN-PT$.

Statement "A" per telecon Dr. Steven Fishman. Office of Naval Research/code 1131.

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PMN-PT COMPOSITIONS

x = 0.03	.97 Pb(Mg _{1/3} Nb _{2/3})O ₃ -.03 PbTiO ₃	≡	.97 PMN-.03 PT
x = 0.05	.95 Pb(Mg _{1/3} Nb _{2/3})O ₃ -.05 PbTiO ₃	≡	.95 PMN-.05 PT
x = 0.07	.93 Pb(Mg _{1/3} Nb _{2/3})O ₃ -.07 PbTiO ₃	≡	.93 PMN-.07 PT

Modification with La³⁺ results in reduced PbO volatility, decreased T_m (~ 25°C/mol%) and inhibits grain growth. Also of great importance is that this modification allows for an examination of the intrinsic relaxor behavior and for obtaining enhanced electrostrictive response with reduced temperature dependence by broadening the macro-micro polar region. Dopants on the A-site such as K⁺, Sr²⁺, and La³⁺ provide compositional variability to examine features of relaxor commonality as the T_m is shifted.

(b) La-Modified PMN-PT

General Formula: (1-x) (Pb_{1-1.5y}La_y□_{0.5y})(Mg_{1/3}Nb_{2/3})O₃-xPbTiO

La-MODIFIED PMN-PT COMPOSITIONS

x = .07, y = 0.01	.93(Pb _{.985} La _{0.01} □ _{0.005})(Mg _{1/3} Nb _{2/3})O ₃ -.07 PbTiO ₃	≡	.93PLMN-.07PT
x = .35, y = 0.07	.65(Pb _{.895} La _{0.07} □ _{0.035})(Mg _{1/3} Nb _{2/3})O ₃ -.35 PbTiO ₃	≡	.07/.65PLMN-.35PT

(c) Sr-Modified PMN-PT

General formula: (Pb_{1-y}Sr_y)[1-x(Mg_{1/3}Nb_{2/3})-xTi]O₃

Sr-MODIFIED PMN-PT COMPOSITIONS

x = .07,	y = .01	(Pb _{0.99} Sr _{0.01})[.93(Mg _{1/3} Nb _{2/3})-.07 Ti]O ₃
x = .07,	y = .03	(Pb _{0.97} Sr _{0.03})[.93(Mg _{1/3} Nb _{2/3})-.07 Ti]O ₃
x = .07,	y = .05	(Pb _{0.95} Sr _{0.05})[.93(Mg _{1/3} Nb _{2/3})-.07 Ti]O ₃

(d) K and La-Modified PMN-PT

(Pb_{0.98}La_{0.01}K_{0.01})[0.93(Mg_{1/3}Nb_{2/3})-.07 Ti]O₃

B. $Pb(Ni_{1/3}Nb_{2/3})O_3-PbTiO_3-PbZrO_3$ (PNN-PT-PZ)

As an alternative to the PMN-PT family PNN-PT-PZ was also selected for the following reasons:

- To examine the "commonality" of relaxor characteristic behavior for a given T_{max} .
- To enhance perovskite formation (pyrochlore elimination) owing to the lower T_m for $Pb(Ni_{1/3}Nb_{2/3})O_3$ (-100°C) and requiring more $PbTiO_3$ (and/or $PbZrO_3$) to shift T_m upwards.

(a) $Pb(Ni_{1/3}Nb_{2/3})O_3-PbTiO_3$ (PNN-PT)

PNN-PT COMPOSITIONS

.85 $Pb(Ni_{1/3}Nb_{2/3})O_3$ -.15 $PbTiO_3$	≡	.85 PNN-.15 PT
.80 $Pb(Ni_{1/3}Nb_{2/3})O_3$ -.20 $PbTiO_3$	≡	.80 PNN-.20 PT
.75 $Pb(Ni_{1/3}Nb_{2/3})O_3$ -.25 $PbTiO_3$	≡	.75 PNN-.25 PT

(b) $Pb(Ni_{1/3}Nb_{2/3})O_3-PbTiO_3-PbZrO_3$ (PNN-PT-PZ)

PNN-PT-PZ COMPOSITIONS

.80 $Pb(Ni_{1/3}Nb_{2/3})O_3$ -.20 $Pb(Zr_{0.53}Ti_{0.47})O_3$
.75 $Pb(Ni_{1/3}Nb_{2/3})O_3$ -.25 $Pb(Zr_{0.53}Ti_{0.47})O_3$
.70 $Pb(Ni_{1/3}Nb_{2/3})O_3$ -.30 $Pb(Zr_{0.53}Ti_{0.47})O_3$

C. Type II . PLZT Type II Relaxors

The PLZT phase diagram indicates that there is a region of pseudocubic symmetry with "slim-loop" P-E ferroelectric hysteresis response. Within this region compositions do not possess permanent remanent polarization at room temperature. However, under the influence an electric field, they do exhibit substantial induced polarization brought about by a PE-FE phase change. The adding of La^{+3} results in a decreased stability of the ferroelectric (macro-polar) rhombohedral or tetragonal phases and a reduction of the T_m (37°C/mol%).⁽⁵⁾

For PLZT (x/65/35) ceramics, addition of 9% La^{+3} is sufficient to reduce the stable region of the FE rhombohedral phase to lower temperatures so that the ceramic compositions we have selected are also Group. I. Electrostrictive materials.

PLZT

General formula: $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\square_{x/4}\text{O}_3$

PLZT Compositions

PLZT (9/65/35)
PLZT (10/65/35)
PLZT (11/65/35)

Commercially available specimens of PLZT will also be obtained for comparison with inhouse produced materials.

Processing

The relaxor compositions proposed above are prepared by solid state reaction via the mixing/milling route. (3) With all these compositions the B-site precursors are prepared first, then the appropriate amounts of PbO , TiO_2 , SrO , La_2O_3 , K_2O , etc. are added after precursor calcination. The component oxides selected offer ease of dispersability in aqueous solution and have minimal moisture absorption. Suppliers for the various reagent grade and high purity materials are listed in Table I. The processing procedure for this is as follows: the precursor powders are mixed together, milling solvent (usually deionized H_2O) is added at about 25 vol% solids along with Tamol 901 dispersant. In order to enhance reactivity and insure homogeneity by this "wet" processing, the prepared slurries employ steric hindrance (polyelectrolyte dispersant) and electrostatic repulsion (pH adjustment by ammonia). The prepared powders are then subsequently SWECO-milled with ZrO_2 media for 18 to 20 hrs., thoroughly dried, and calcined. The calcined powder is hammer-milled and then the rest of the ingredients are added. The milling step is performed again with ZrO_2 media overnight, redried, and recalcined.

Calcination temperatures: B-site Precursors: 1. Both $(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_2$ and $(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_2$
→ 1400°C/4 hrs
 $\text{MgNb}_2\text{O}_6 + \text{MgTa}_2\text{O}_6 \rightarrow 1100^\circ\text{C}/4 \text{ hrs}$
 $\text{NiNb}_2\text{O}_6 \rightarrow 1100^\circ\text{C}/4 \text{ hrs}$
with PbO 2. 700°C PMN, PNN-PT, PMN-PT
825°C-850°C → PLZT, PNN-PT

23 x 75 x 50 mm. 4

TABLE I.
Component Oxide Powders Used in Synthesis of Selected Materials.

Reagent Grade Materials		
Material	Grade	Supplier
2 PbCO ₃ -Pb(OH) ₂ (white)	99%	Hammond Lead Products, Inc. P.O. 6408, Hammond, IN 46325
MgCO ₃ -Mg(OH) ₂	99%	Fischer Scientific Co. 585 Alpha Dr., Pittsburgh, PA 15238
NiO	99%	Fischer Scientific Co. 585 Alpha Dr., Pittsburgh, PA 15238
Nb ₂ O ₅	99.5%	Fansteel Metals Co., One Tantalum Place North Chicago, IL 60064
TiO ₂	99%	Whittaker, Clark, and Daniels, Co. 1000 Coolidge St., S. Plainfield, NJ
SrCO ₃	99%	Alfa Products Co. 152 Andover St., Danvers, MA 01923
ZrO ₂	99%	Harshaw Chemical Company
High Purity Grade Materials		
PbO (yellow)	Grade 1, 99.999%	Johnson Matthey, Inc. Seabrook, NH 03874
MgCO ₃	99.999%	Johnson Matthey, Inc. Seabrook, NH 03874
Nb ₂ O ₅	99.999%	Johnson Matthey, Inc. Seabrook, NH 03874
La ₂ O ₃	99.9%	Alfa Products Co. 152 Andover St., Danvers, MA 01923

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